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(54) CONDUCTIVE RESIN SHEET FOR ELECTRODE OF BATTERY AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a conductive resin sheet for battery electrode embodied in a light construction, having excellent chemical resistance, and good conductivity.

SOLUTION: The conductive resin sheet of battery electrode is formed from a thermplastic resin containing conductive particles, wherein the volume specific resistance of the resin sheet is below 100 Ω.cm while the water vapor permeability is below 50 g/(m2.day), and at least to its one surface an electrode active material is attached.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention is lightweight and relates to a conductive resin sheet for cell electrodes excellent in chemical resistance and conductivity, and a manufacturing method for the same.
It is related with the method of manufacturing the conductive resin sheet for cell electrodes which has the outstanding quality with this invention preferred as an electrode material of a lead storage battery, and the conductive resin sheet for the still more detailed cell electrodes.

[0002]
[Description of the Prior Art]Conventionally, the metallic foil, a board and a metallic mesh, and the lattice are used for the cell electrode.
A lead lattice is used in a lead storage battery, and aluminum foil and copper foil have been used in the lithium ion battery.
On the other hand, in order to raise the weight energy density of a cell, the lattice for electrodes with which the weight saving was made is proposed by JP,10-188996,A. This lattice for electrodes provides the current carrying part which becomes a mesh shape thing which consists of glass fibers etc. from lead or a lead alloy.
[0003]
[Problem(s) to be Solved by the Invention]However, the following faults existed in such a conventional cell electrode. That is, although a metallic foil, a board, a mesh, and a lattice had the outstanding conductivity, density of metal was large as compared with resin, and when a metallic material was used as an electrode material of a cell, the electric generating power per weight of a cell was small. Furthermore, with the lead storage battery, it corroded, when the electrode material which consists of metal lead repeated charge discharge of a cell, and this

had become an obstacle which develops the life of a cell.

[0004]The case of the lattice for electrodes proposed by JP,10-188996,A also had the technical problem that the metal material as a conductive member is required similarly since it constitutes from a member of non-electrical conductivity, and electrode weight was still heavy.

[0005]The purpose of this invention cancels the fault of the above-mentioned conventional technology, is lightweight, and there is in providing a conductive resin sheet for cell electrodes excellent in the chemical resistance which can be used for a lead storage battery, and conductivity, and a manufacturing method for the same.

[0006]

[Means for Solving the Problem]As a result of inquiring wholeheartedly in view of a problem mentioned above, this invention persons contain a conductive particle, find out that said problem is solvable by making an electrode active material hold to a thermoplastic resin sheet with specific volume ratio resistance and water-vapor-permeation nature, and came to make this invention.

[0007]Namely, a conductive resin sheet for cell electrodes of this invention, It is a conductive resin sheet which consists of thermoplastics containing a conductive particle, Volume resistivity of this conductive resin sheet is 100 or less ohm-cm, moisture vapor transmission is 50g / (m^2 and day) following, and it is a conductive resin sheet for cell electrodes making an electrode active material come to adhere to the single surface at least.

[0008]A manufacturing method of a conductive resin sheet for cell electrodes of this invention, A thermoplastic resin composition containing a conductive particle is extruded from a cap to a sheet shaped with an extrusion machine at least, It is a manufacturing method of a conductive resin sheet for cell electrodes consisting of a process of carrying out cooling solidification and obtaining a conductive resin sheet with a cooling medium, and a process which makes an electrode active material stick to the surface of an obtained conductive resin sheet by pressure.

[0009]

[Embodiment of the Invention]Hereafter, the desirable embodiment of this invention is described.

[0010]the conductive resin sheet whose moisture vapor transmission of the conductive resin sheet for cell electrodes in this invention volume resistivity is 100 or less ohm-cm, and is 50g / (m^2 and day) following -- an electrode active material is made to adhere to a single surface at least

[0011]In this invention, a weight saving can be attained by using the subject of a conductive resin sheet as thermoplastics rather than the metallic material which is the conventional electrode collector material, and it becomes possible to raise the weight energy density of a cell by using this.

[0012]Although the conductive resin sheet for cell electrodes of this invention comprises a conductive thermoplastic resin sheet (conductive resin sheet) and electrode active material in this way, The moisture vapor transmission of this conductive resin sheet portion needs to be 50g / (m^2 and day) following, and is 40g / (m^2 and day) following preferably. When moisture vapor transmission exceeds this, it becomes easy to generate evaporation of an electrolysis solution, the leakage of an active material, etc., and when a cell is constituted, fault occurs. Although moisture vapor transmission is so preferred that the value is small and moisture vapor transmission can be made small by increasing sheet thickness, since electrode weight also increases by increasing sheet thickness, as for the value, 1g/(m^2 and day) becomes a minimum mostly.

[0013]The volume resistivity of the thermoplastic resin sheet portion of the conductive resin sheet for cell electrodes of this invention needs to be below 100ohm and cm. When volume resistivity exceeds 100 ohm-cm, the voltage drop of a cell is large and power loss becomes large. Volume resistivity is so preferred that it is small, and it is preferred that they are 10 or less ohm-cm and 1 more ohm-cm or less. In order to make volume resistivity small, it is effective to raise the content of a conductive particle, but if this content is raised recklessly, shaping of the sheet itself will become difficult and it will become easy to generate the defect of a pinhole etc. About 0.01 ohm-cm of volume resistivity is a limit substantially. In order to attain such volume resistivity, it is preferred to make content of the conductive particle to thermoplastics into 10 % of the weight or more, and 15 to 60% of the weight of the range is preferred from a point of conductivity and sheet forming nature.

[0014]It is preferred to use at least one kind selected from carbon, metal, and metallic compounds as a conductive particle which thermoplastics is made to contain. As carbon, carbon black and graphite can be used preferably and titanium, copper, lead, zinc, or solder can be mentioned as metal. Furthermore as metallic compounds, at least one kind selected from tin oxide, indium oxide and Ti, Zr, V, Nb, Ta, Cr, Mo, the carbide of at least one kind of metal chosen from W, the nitride, the boride, and the silicide can be used. TiC, TiN, TiB_2, or $TiSi_2$ which is carbide of tin oxide or Ti, a nitride, a boride, and a silicide is especially preferred. ** et al. -- ** -- even when a conductive particle is independent -- ** et al. [or] -- ** -- it does not matter even if it mixes and uses particles by arbitrary ratios.

[0015]Although there is no limitation in particular in the particle diameter of a conductive particle, from a point of the dispersibility within thermoplastics, it is preferred that it is the range of 0.01-10 micrometers, and the range of it is 0.05-5 micrometers more preferably.

[0016]The conductive particle should just have conductivity in a particle surface, and the conductive substance may have wrap core shell structure for the particle surface. Specific gravity of a conductive substance may be high, and even if the specific gravity of the

conductive particle itself can be reduced by considering it as core shell structure and it makes thermoplastics contain this conductive particle with high content, a lightweight conductive resin sheet is obtained. If the shape of a conductive particle is needlelike, high conductivity will be obtained with smaller particle weight. In this case, it is preferred that the ranges of a particle major axis / particle minor-axis ratio are 5-50, and the ranges of it are 10-30 more preferably. When an acicular particle-shaped effect does not show up easily in less than five and this ratio exceeds 50, it becomes easy to condense particles in thermoplastics. When the conductive substance itself cannot make needlelike structure easily, a needlelike conductive particle can be obtained by, for example, considering it as the core shell structure which covered the conductive substance on the acicular particle surfaces, such as potassium titanate.

[0017]Although the thickness in particular of the conductive liner sheet for cell electrodes of this invention is not limited, if too thin, the handling in the case of battery manufacturing will become difficult, and since the weight per sheet unit area will increase if too thick, the effect of the improvement in weight energy density at the time of using it for a cell becomes small. for this reason, it is a range which it is preferred that it is the range of 20-1000 micrometers as for the thickness of the conductive resin sheet portion except an electrode active material, and is 50-800 micrometers especially -- it is desirable.

[0018]Even if the conductive liner sheet for cell electrodes of this invention has few conductive thermoplastic resin sheets, it makes an electrode active material adhere to a single surface.

[0019]The electrode active material used in this invention refers to the substance which participates in the chemical reaction of a cell, and lead oxide is used in an anode in a lead storage battery, and metal lead is used in a negative electrode. As lead oxide, the porous body which consists of granular materials is used preferably.

[0020]As for the electrode active material which constitutes the conductive resin sheet for cell electrodes of this invention, it is preferred that they are lead metal and/or lead oxide. That is, it is preferred to use the conductive resin sheet for cell electrodes of this invention for the electrode for lead storage batteries.

[0021]The quantity which makes an electrode active material adhere to a conductive thermoplastic resin sheet, Although it changes with capacity for which a cell is needed and there is no limitation in particular, from the handling nature of an electrode sheet, and a viewpoint of a cell weight saving, it is preferred that it is within the limits of 0.1 mm - 5 mm as thickness of the electrode sheet to which the active material was made to adhere, and the ranges of it are 0.3 mm - 3 mm more preferably. As a method of making an electrode active material adhering to a conductive resin sheet, Since the electrode active material fabricated to the sheet shaped can be made to adhere to a conductive resin sheet by being stuck by pressure with a press etc., it may heat even if it performs sticking by pressure at ordinary temperature, and it may carry out and the thermoplastics of the conductive resin sheet of this

invention itself is a subject, An electrode active material can be bonded by thermo-compression near the softening temperature of this thermoplastics. For example, if an electrode active material is a lead sheet, it can make it bond by thermo-compression a conductive resin sheet and directly, and if an electrode active material is lead oxide, What is necessary is to sheet-ize this, to dry, to create [to carry out the mix of the dilute sulfuric acid beforehand to create the paste of lead oxide,] a lead oxide active material board, and just to stick this by pressure with a conductive resin sheet.

[0022]In this invention, there is no limitation in particular in the thermoplastics which constitutes a conductive resin sheet, For example, although polyethylene, polypropylene, a polymethylpentene, polystyrene, polyphenylene SURUFAIDO, polyvinyl chloride, polyethylene terephthalate, etc. can be used, The resin which consists of polyethylene, polypropylene, polystyrene, and these copolymers is especially used preferably from a chemical-resistant viewpoint.

[0023]In this invention, the conductive resin sheet can take the composition which carries out the two-layer owner of the layer from which the kind of conductive particle to contain differs at least. Especially in such composition, the layer containing the particles which are excellent in chemical resistance is used for the active material, i.e., electrolysis solution, side, and though it is inferior to chemical resistance, the sheet which reconciled chemical resistance and conductivity on the high level can be obtained by using for the layer containing particles excellent in conductivity current collection-side. In this case, what is necessary is for there to be no limitation in particular in the thickness ratio of each class, and just to make it laminate by arbitrary ratios.

[0024]The conductive resin sheet for cell electrodes should just make an electrode active material adhere to at least one side of a conductive resin sheet, when it constitutes a single electrode, but. When it constitutes a unit battery cell from a form connected in series, the object for anodes and the electrode active material in which the kinds for negative electrodes differ can be made to adhere to the rear surface of a conductive resin sheet, respectively.

[0025]The manufacturing method of the conductive resin sheet for cell electrodes of this invention, Comprise at least two processes and one extrudes the thermoplastic resin composition containing a conductive particle from a cap to a sheet shaped with an extrusion machine, It is the process of carrying out cooling solidification and obtaining a conductive resin sheet with a cooling medium, and the 2nd is a process which makes an electrode active material stick to the obtained conductive resin sheet surface by pressure. In the former process, as a cooling medium, it is preferred that they are a metal drum and a metallic roll, and it is preferred to take the structure where the fluid for cooling flows into these insides. The temperature of the surface of a drum or a roll can be adjusted by adjusting the temperature of the fluid for cooling. In order to obtain the conductive resin sheet which was excellent in

smoothness, it is required to stick these cooling media and the extruded molten resin sheet, but for the purpose, conventionally publicly known methods, such as an air knife, an air chamber, a nip roll, or an electrostatic seal-of-approval method, can be used.

[0026]When using polyolefin resin as thermoplastics, an air knife method or an air-chamber method is used preferably. When the conductive resin sheet portion of the conductive resin sheet for cell electrodes is constituted above two-layer, The thermoplastic resin composition in which the kinds of conductive particle contained in two or more sets of each extrusion machines differ can be supplied, each melting resin can be introduced into a laminated block or a lamination cap after melting extrusion, and it can manufacture by the method of performing lamination more than two-layer.

[0027]Since the thermoplastics which contained the conductive particle in high concentration is inferior to a moldability, the conductive resin sheet of the thickness for which it asks only by melting extrusion may not be obtained. In this case, after obtaining a conductive resin sheet, it can adjust to desired thickness by rolling pressurizing this conductive resin sheet between rolls.

[0028]The thermoplastic resin composition containing a conductive particle can be obtained by carrying out melt kneading of the conductors, such as carbon black, to resin, such as polyethylene, for example. Of course, other additive, for example, antiblocking agent, extender, stabilizer, antioxidant, adhesiveness-reducing and a thickener, particle dispersing agent, and other resin can be added if needed. A publicly known device can be used for melt kneading from the former, such as a biaxial kneading machine.

[0029]Thus, the obtained conductive resin sheet for cell electrodes has the outstanding conductivity and chemical resistance, and they can be preferably used for it as an electrode of a cell. The weight energy density of a cell can be raised by using the conductive resin sheet for cell electrodes of this invention for a lead storage battery. The conductive resin sheet for cell electrodes of this invention is possible also for performing heat adhesion by applying heat, can make a battery cell container able to carry out heat adhesion of the conductive resin sheet for these cell electrodes itself, and can also constitute an encapsulated type battery.

[0030][Measuring method of physical properties] Next, the measuring method used by this invention is described.

[0031]1. The volume resistivity JIS-K7194 method of the sheet was followed and it measured by four probes.

[0032]2. The moisture-vapor-transmission JIS-K7129 method was followed and it measured on condition of RH by product PERMATRAN-Wmade from Modern Controls Inc 3/30 25**0.5 ** and relative humidity 90**2%.

[0033]3. Particle shape particles were observed with the scanning electron microscope or the transmission electron microscope, the major axis and minor axis of particles were measured, it

asked for the ratio of the particle major axis / particle minor axis, and the average value per 1,000 particles was calculated.

[0034]4. Particle diameter particles were observed with the scanning electron microscope or the transmission electron microscope, it asked for the diameter of circle which has an area equal to the cross-section area of particles, and the average value per 1,000 particles was calculated.

[0035]

[Example]An example explains this invention still in detail.

[0036][Example 1] Low-density-polyethylene 65 weight section and carbon black particle 35 weight section whose particle diameter is 0.02 micrometer were mixed, with the biaxial kneading machine, melt kneading was carried out and the conductive resin composition was obtained. This resin composition was supplied to the extrusion machine with a cylinder diameter of 90 mm, and was extruded from a T die melting extrusion and 400 mm in width to metal drum lifting as a melting sheet at 250 **. 500 mm in diameter and the skin temperature of a metal drum are 60 **.

The melting sheet was stuck to the metal drum with the air knife.

Thus, in 100 micrometers and volume resistivity, thickness obtained the conductive resin sheet 5 ohm-cm and whose moisture vapor transmission are 10g/(m^2 and day).

[0037]Next, 5 mm of conductive resin sheet outsides were left and laid on top of the single surface of the conductive resin sheet of the 10-cm angle which obtained previously the lead sheet with a thickness of 500 micrometers of a 9-cm angle, it pressed by the pressure of 1MPa with the temperature of 120 **, and the 600-micrometer-thick electrode sheet for lead battery negative electrodes was obtained.

[0038][Example 2] Volume resistivity obtained the conductive resin sheet 12g/(m^2 and day) and whose thickness 15 ohm-cm and moisture vapor transmission are 100 micrometers like Example 1 except having changed the carbon black particle into the tin dioxide with a particle diameter of 0.02 micrometer. Sulfuric acid solution 30 weight section and lead oxide 70 weight section were mixed 30 more%, the lead oxide paste was created by often kneading, and the 500-micrometer-thick lead oxide board was obtained by slushing into a mold and drying it. Thus, the conductive resin sheet containing the lead oxide board of a 9-cm angle and the tin dioxide of a 10-cm angle which were obtained was piled up, it pressed by the pressure of 1MPa with the temperature of 120 **, and the 600-micrometer-thick electrode sheet for lead battery anodes was obtained.

[0039]The obtained electrode sheet was lighter-weight than metal electrodes. Next, when sulfuric acid of concentration was used as the electrolysis solution 30%, the negative electrode and the sheet of this example 2 were used as the anode for the sheet of Example 1, heat adhesion of the peripheral part of each electrode was carried out at the battery container made

from polypropylene and the sealed lead acid battery was constituted, the weight energy density of the cell also improved. The corrosion of each electrode was not seen even after the charge and discharge of a cell.

[0040][Comparative example 1] The resin composition which made the rate of a compounding ratio of Example 1 carbon black 65 weight section and low-density-polyethylene 35 weight section was obtained. Since this resin composition was not able to do melting extrusion, it pressed by the pressure of 5MPa by the state where it heated at 280 **, and the 100-micrometer-thick sheet was obtained. Although the volume resistivity of this sheet was 0.1 ohm-cm, moisture vapor transmission was 100g/(m^2 and day). The tin dioxide sheet was made to stick by pressure like Example 2, and the sheet for cell electrodes was obtained. Although the anode of Example 2 was replaced with the sheet of this comparative example 1 and the cell was constituted, the leakage of an electrolysis solution occurred.

[0041][Example 3] except having used the conductive resin composition in which particle diameter changed tin dioxide particles into 2 silicification titanium ($TiSi_2$) which is 2 micrometers, Like Example 2, volume resistivity included 1 ohm-cm, in moisture vapor transmission, 20g/(m^2 and day) and conductive resin sheet thickness included 100 micrometers and an active material, and the conductive resin sheet for cell electrodes which is a thickness of 600 micrometers was obtained. Furthermore this sheet was used as the anode and the lead storage battery was constituted by using the sheet of Example 1 as a negative electrode. The weight energy density of the cell also improved. The corrosion of each electrode was not seen even after the charge and discharge of a cell.

[0042][Example 4] The conductive resin composition which used the conductive resin composition used in Example 1 from the 1st extrusion machine in Example 3 from the 2nd extrusion machine was extruded at the temperature of 250 **, respectively, and it laminated to two-layer by the laminated block.

[0043]The laminated molten resin sheet was extruded from the 400-mm-wide T die to metal drum lifting as a melting sheet. 500 mm in diameter and the skin temperature of a metal drum are 60 **.

The melting sheet was stuck to the metal drum with the air knife.

Thus, in 100 micrometers and volume resistivity, thickness obtained the conductive resin sheet 3 ohm-cm and whose moisture vapor transmission are 15g/(m^2 and day). The layer (2 silicification titanium layer) with which the layer (carbon layer) with which this conductive resin sheet blended carbon blended 75 micrometers and 2 silicification titanium was 25 micrometers. Next, the lead sheet with a same thickness [the / as Example 1] of 500 micrometers was stuck to the carbon layer side by pressure, the 500-micrometer-thick lead oxide sheet was made to adhere to the 2 silicification titanium layer side, and total thickness

obtained the electrode sheet which is 1100 micrometers. Thus, the sheet of Example 1 and the sheet of Example 3 were combined, and the cell unit cell constituted the lead storage battery by which a two-piece series connection was carried out. The corrosion of each electrode was not seen even after the charge and discharge of a cell.

[0044][Example 5] except the particle major axis / minor-axis ratio having made the particles which coated with the tin dioxide the needlelike titanium oxide surface with a major axis of 3 micrometers which is 14 contain 20% of the weight, The sheet for cell electrodes (conductive resin sheet 100 micrometers in thickness, and lead oxide sheet 500 micrometers in thickness) whose volume resistivity is 10 ohm-cm and whose moisture vapor transmission is 15g/(m^2 and day) like Example 2 was obtained. The sheet of this Example 5 was combined by having used the anode and the sheet of Example 1 as the negative electrode, and the lead battery was constituted. The corrosion of each electrode was not seen even after the charge and discharge of a cell.

[0045]

[Effect of the Invention]According to this invention, since it is lightweight, the cell electrode excellent in chemical resistance and conductivity is obtained and the weight saving of a cell is attained, especially the weight energy density of a lead storage battery can be raised.

[Translation done.]

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CLAIMS

[Claim(s)]
[Claim 1]It is a conductive resin sheet which consists of thermoplastics containing a conductive particle, A conductive resin sheet for cell electrodes which volume resistivity of this conductive resin sheet is 100 or less ohm-cm, and moisture vapor transmission is 50g / (m^2 and day) following, and is characterized by making an electrode active material come to adhere to the single surface at least.
[Claim 2]The conductive resin sheet for cell electrodes according to claim 1 containing at least one kind of conductive particle selected from carbon, metal, and metallic compounds 10% of the weight or more as a conductive particle.
[Claim 3]The conductive resin sheet for cell electrodes according to claim 2, wherein metallic compounds are tin oxide or/and indium oxide.
[Claim 4]Carbide of at least one kind of metal in which metallic compounds were chosen from Ti, Zr, V, Nb, Ta, Cr, Mo, and W, The conductive resin sheet for cell electrodes according to claim 2 being at least one kind of metallic compounds chosen from either a nitride, a boride and a silicide.
[Claim 5]The conductive resin sheet for cell electrodes according to any one of claims 1 to 4, wherein a conductive particle has core shell structure.
[Claim 6]The conductive resin sheet for cell electrodes according to any one of claims 1 to 5, wherein a conductive particle is acicular shape and ranges of its particle major axis / particle minor-axis ratio are 5-50.
[Claim 7]The conductive resin sheet for cell electrodes according to any one of claims 1 to 6, wherein electrode active materials are lead metal and/or lead oxide.
[Claim 8]The conductive resin sheet for cell electrodes according to any one of claims 1 to 7, wherein resin which constitutes a conductive resin sheet is at least one kind of resin selected from polyethylene, polypropylene, polystyrene, and these copolymers.

[Claim 9]The conductive resin sheet for cell electrodes according to any one of claims 1 to 8 carrying out the two-layer owner of the layer from which a kind of conductive particle to contain differs at least.

[Claim 10]The conductive resin sheet for cell electrodes according to any one of claims 1 to 9 making an electrode active material different, respectively come to adhere to a rear surface of a conductive resin sheet.

[Claim 11]A thermoplastic resin composition containing a conductive particle is extruded from a cap to a sheet shaped with an extrusion machine at least, A manufacturing method of a conductive resin sheet for cell electrodes consisting of a process of carrying out cooling solidification and obtaining a conductive resin sheet with a cooling medium, and a process which makes an electrode active material stick to the surface of an obtained conductive resin sheet by pressure.

[Claim 12]A manufacturing method of the conductive resin sheet for cell electrodes according to claim 11 which supplies a thermoplastic resin composition in which kinds of conductive particle contained in two or more sets of each extrusion machines differ, introduces each melting resin into a laminated block or a lamination cap after melting extrusion, and is characterized by performing lamination more than two-layer.

[Claim 13]A manufacturing method of the conductive resin sheet for cell electrodes according to claim 11 or 12 characterized by making sheet thickness thin with rolling after obtaining a conductive resin sheet.

[Translation done.]